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(54) Flame-retardant polyester moulding compositions

(57) A moulding composition consists of a thermoplastic polyester such as polyethylene terephthalate or polybutylene terephthalate together with reinforcing fibres and, as fire retardant system, red phosphorus with melamine cyanurate. The reinforcing fibres are preferably glass fibres. The red phosphorus may be carried on a polymeric carrier and/or encapsulated with a polymer e.g. a polyamide. Optional ingredients include a filler and a nucleant. The compositions have enhanced flame retardancy and electrical tracking resistance.

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Improvements in or relating to polyester compositions

This invention relates to polyester compositions, and particularly to those based on thermoplastic polyesters such as polyethylene terephthalate (PET) and polybutylene terephthalate.

Thermoplastic polyesters are commonly used in moulding compositions, and when flame retardant grades are required they are typically flame retarded with additives containing halogens. The level of flame retardancy obtained from such materials can be very good and VO ratings in the Underwriters (UL) Flammability test are readily achieved. A problem with such compositions, however, is that the resistance to electrical tracking of thermoplastic polyesters containing these additives is very low. (Typical values of Comparative Tracking Index - CTI - for a UL VO material would be around 200 volts.)

It has also been proposed to use red phosphorus as a flame retardant in PET and PBT compositions, whereby some improvement in electrical tracking resistance may be achieved.

US Patent No 4,314,927 proposes the use of red phosphorus and melamine cyanurate in moulding compositions of Nylon 66 to improve the heat stability and lower the level of phosphorus required to achieve V0 ratings. It gives no guidance as to the electrical tracking resistance of the compounds disclosed.

We have now found that red phosphorus and melamine cyanurate may be used together in glass reinforced thermoplastic polyester compositions to enhance both flame retardancy and electrical tracking resistance.

Thus according to the present invention a polyester moulding composition comprises a thermoplastic polyester, reinforcing fibres and as fire retardant red phosphorus with melamine cyanurate.

The thermoplastic polyester may be, for example, polyethylene terephthalate (PET) or polybutylene terephthalate (PBT) or a polyester containing at least 80 per cent by weight of repeating units derived from ethylene terephthalate or butylene terephthalate.

The amount of thermoplastic polyester in the composition is preferably in the range 35 to 75 per cent by weight of the total composition.

As flame retardant red phosphorus is an essential ingredient of the polyester moulding composition but the red phosphorus is preferably treated in order to reduce its handling difficulties, since red phosphorus alone can be very dangerous in handling. Thus the red phosphorus may be carried on a polymeric carrier, and/or may be encapsulated with a suitable substance such as a polymer or resin.

Preferably the amount of red phosphorus in the composition is 1 to 15 per cent by weight of the total composition.

The composition contains reinforcing fibres, for example short lengths of inorganic reinforcing fibre such as glass fibre, although other types of fibre which will stand up to the processing conditions to which the composition is subjected may be used. The amount of reinforcing fibre in the composition is preferably in the range 15 per cent to 45 per cent by weight of the composition.

Fillers may also be used in the composition, for example kaolinitic clays, talc, glass spheres, wollastonite, calcium carbonate, and when used in conjunction with the

reinforcing fibres have the advantage of giving a composition with less warping and less anisotropic properties.

The composition may also contain a nucleant and the nucleant may be either a metal salt of an organic acid, for example a metal stearate, acetate or benzoate, or a finely divided material which does not melt at or below the melting point of polyethylene terephthalate, for example microtalc. The preferred nucleant is a group 1 metal stearate, or microtalc with a particle size of less than 20 microns.

Preferably the group 1 metal stearate is sodium stearate, which is a known nucleant for polyethylene terephthalate and gives easier nucleation of the polyester. The nucleant is preferably used in an amount no more than 1% by weight of the composition, particularly in the range 0.1 to 0.7 per cent by weight. However, if a finely divided solid nucleant is used it may be used in greater proportion, eg up to six parts by weight per 100 parts by weight total polymer, and may be used, if desired, in addition to a nucleant of the other type.

In the compositions of this invention the melamine cyanurate functions to enhance the flame retardancy of the system with an important improvement in the electrical

tracking resistance of the moulded composition. The amount of melamine cyanurate used may be in the range from 1 per cent to 20 per cent, preferably 4 per cent to 15 per cent, by weight of the composition.

Other additives such as mould release agents, stabilisers etc may be used in the composition as desired.

The invention will now be described in more detail, by way of example only, by means of the following Examples.

EXAMPLES

Flammability Testing

The method used was the standard Underwriters Laboratories test method UL94. V0 means that the specimens burnt for less than 10s after removal of flame, that the total burn time for ten applications of the flame on five specimens was less than 50 seconds. In addition no flaming drops are permitted. In V1 classification no specimen burns for longer than 30 seconds after the application of the flame and the total burning time for 10 specimens is less than 250 seconds. No flaming drops are permitted. The same criteria apply in V2 classification except that some flaming drops are permitted.

In addition to these classifications, the average burning time for each application of flame was calculated and the occurrence of non-flaming drops was noted (10 specimens).

Electrical Tracking Resistance Testing

The test equipment used is that of the Comparative Tracking Index test of the European Standard IEC 112 (DIN 53480). An aqueous solution containing 0.1% NH_4Cl was dropped at 30 second intervals on to the surface of the mouldings between two electrodes carrying the applied voltage. Platinum electrodes were used, with trips at 0.5 amps and 2 secs.

Results are expressed in the tables below for each applied voltage as "failures", or "passes" at 50 drops total.

Examples 1 and 2

Two compositions of polyethylene terephthalate (PET) were prepared with and without melamine cyanurate for comparison.

The compositions were made by first blending the ingredients shown (as parts by weight) in Table I, and then fully compounded in a Baker Perkins twin-screw extruder.

TABLE I

Ingredient	Example 1	Example 2
PET (D217)	60	50
Coated Red Phosphorus	7.2	7.2
Glass Fibre	30	30
Nucleant/Mould Release Agent	3	3
Melamine Cyanurate "C"	0	10
Stabiliser	0.25	0.25

In each example the red phosphorus used (MASTERFLAM P70S) was encapsulated in a polyamide carrier (70% by weight of red phosphorus). The glass fibres were grade 429YZ from Owens Corning Fibreglass, chop length 4.5mm. The nucleant/mould release agent was NAI/LOXIOL masterbatch and the stabiliser was IRGAFOS PEPQ. NAI - is a nucleant/polymer (linear low density polythene) supplied by Goodyear. LOXIOL is pentaerythritol tetrastearate supplied by Henkel.

Sample mouldings were made by injection moulding from each composition on a standard BIPEL 60/26 machine using a barrel temperature of 270°C.

These were tested for flammability and for Electrical Tracking Resistance. The results of these tests are given below in Table II.

TABLE II

Test	Example 1	Example 2
Flammability - UL94 test		
a) At 1.5mm		
Class	V0	V0
Average Burn Time (secs)	0.7	0
b) At 3mm		
Class	V0	V0
Average Burn Times (secs)	0.1	0
Electrical Tracking Resistance		
At 400V	Fail (at 6 and 18 drops)	Pass (5 passes at >52 drops)

Examples 3 and 4

Two compositions of polybutylene terepthalate (PBT) were prepared with and without melamine cyanurate for comparison.

The compositions were made by first blending the ingredients shown (as parts by weight) in Table III, and then fully compounded in a Baker Perkins twin-screw extruder.

TABLE III

Ingredient	Example 3	Example 4
PBT (TQ9)	60	50
Coated Red Phosphorus	7.2	7.2
Glass Fibre	30	30
Nucleant/Mould Release Agent	3	3
Melamine Cyanurate "C"	0	10
Stabiliser	0.25	0.25

In each example the red phosphorus used (MASTERFLAM P70S) was encapsulated in a polyamide carrier (70% by weight of red phosphorus). The glass fibres were grade 429YZ from Owens Corning Fibreglass, chop length 4.5mm. The nucleant/mould release agent was NAI/LOXIOL masterbatch and the stabiliser was IRGAFOS PEPQ. NAI is a nucleant/polymer (linear low density polythene) supplied by Goodyear. LOXIOL is pentaerythritol tetrastearate supplied by Henkel. Sample mouldings were made by injection moulding from each composition on a standard BIPEL 60/26 machine using a barrel temperature of 270°C.

These were tested for flammability and for Electrical Tracking Resistance exactly as for Examples 1 and 2. The test results were very similar; Example 3 failed and Example 2 passed.

CLAIMS

1. A polyester moulding composition which comprises thermoplastic polyester, reinforcing fibres and as fire retardant red phosphorus with melamine cyanurate.

2. A moulding composition according to claim 1 in which the thermoplastic polyester is polyethylene terephthalate or polybutylene terephthalate or polyester containing at least 80 per cent by weight of repeating units derived from ethylene terephthalate or butylene terephthalate.

3. A moulding composition according to claim 1 or 2 in which the amount of the thermoplastic in the composition is in the range 35-75 per cent by weight of the total composition.

4. A moulding composition according to any preceding claim in which the amount of red phosphorus in the composition is in the range 1-15 per cent by weight of the total composition.

5. A moulding composition according to any preceding claim in which the amount of reinforcing fibres is in the range 15-45 per cent by weight of the total composition.

6. A moulding composition according to claim 5 in which the reinforcing fibres are inorganic reinforcing fibres such as glass fibres.

7. A moulding composition according to any preceding claim which additionally comprises at least one filler.

8. A moulding composition according to any preceding claim which also contains a nucleant for the thermoplastic polyester.

9. A moulding composition according to claim 8 in which the nucleant is a Group 1 metal stearate, or micro talc with a particle size of less than 20 microns.

10. A moulding composition according to any preceding claim in which the amount of melamine cyanurate is in the range from 1-20 per cent by weight of the total composition.

11. A moulding composition according to claim 10 in which the amount of melamine cyanurate is in the range 4-15 per cent by weight of the total composition.

12. A moulding composition substantially as described herein in the foregoing Example 2.

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Examiner's report to the Comptroller under Section 17 (The Search Report)

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Relevant Technical fields

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Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES:- DERWENT WPI, WPIL

Documents considered relevant following a search in respect of claims 1 TO 12

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	EP 0019768 A1 (BASF) see the whole specification	1,4 to 7,10,11
X; &	US 4314927 (BASF) see the whole specification	1,4 to 7, 10,11

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

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